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(54) Flame retardant styrene resin composition

Flammgeschützte Styrolharzzusammensetzung

Composition de résine de styrène retardateur de flamme

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Description

The present invention relates to a flame-retardant styrene resin composition having an improved light resistance.

Styrene resins having excellent mechanical and electric properties and moldability are used for various purposes. However, since the styrene resins are flammable, it is eagerly demanded to make them nonflammable and to improve their light resistance when they are used for producing electric components or automobile parts.

Therefore, a flame retardant and a flame retarding assistant are usually added in the production of flame-retardant styrene resins. A halogenous flame retardant and antimony trioxide are most usually used as the flame retardant and the flame retarding assistant, respectively. In using the flame retardant and flame retarding assistant, it was desirea to improve the compatibility and dispersibility of the additives in the resin by reducing the particle size of the additives as far as possible in order to prevent the properties such as mechanical strengths, e.g. tensile strength or impact resistance, of the molding from being impaired. Therefore antimony trioxide in the form of fine particles having an average particle diameter of less than 2 µm, for example, 0.5 µm has been used as the flame retarding assistant.

It is known that when a halogenous flame retardant is added to a flame retardant, various deterioration phenomena such as the formation of a carbonyl group or conjugated double bond, cross-linkage and breakage of the molecular chain are caused by the dehydrohalogenation of the flame retardant due to heat or light to cause coloring or to deteriorate the mechanical strengths. A light stabilizer, ultraviolet absorber, antioxidant, etc. are therefore used.

DD-A-151075 discloses a flame-retardant styrene resin composition. The flame retardant consists of a synergistic mixture of a brominated oligomer of α-methylstyrene and antimony trioxide having a particle size of less than 5 µm.

DD-A-143022 discloses a flame-retardant resin composition based on a styrene polymer. The flame retardant consists of a synergistic mixture of 2,3-dibromobutene-2-diol-1,4 and antimony trioxide having a particle size of less than 5 µm.

However, it was found that the coloring of a known flame-retardant styrene resin containing antimony trioxide as the flame retarding assistant was accelerated by antimony trioxide when the resin was exposed to light.

After intensive investigations made for the purpose of improving the light resistance of a flame-retardant styrene resin composition containing antimony trioxide as the flame redarding assistant, the inventors have found that the light resistance can be remarkably improved without impairing the flame retardancy or mechanical strengths of the molding by providing a flame-retardant styrene resin composition comprising:

- 100 parts by weight of a styrene resin,
- 3 to 50 parts by weight of a halogen-containing flame retardant selected from the group consisting of a brominated bisphenol A epoxy resin, a tetrabromobisphenol A carbonate oligomer, tetrabromobisphenol A and bis(tribromophenoxy)ethane, and
- 0.5 to 15 parts by weight of antimony trioxide having an average size of from 3 to 9 µm.

It is improved in view of weatherability.

The styrene resin is preferably polystyrene, a homopolymer of a styrene compound or a copolymer of styrene or a styrene compound and a co-monomer.

The term "styrene resin" as used in the present invention includes homopolymers and copolymers of styrene or its derivatives such as α-methylstyrene and vinyltoluene; copolymers of these monomers with a vinyl monomer such as acrylonitrile, methyl methacrylate or N-phenylmaleinimide; copolymers of them with a diene rubber such as polybutadiene, ethylene or propylene; and copolymers produced by copolymerizing an ethylene/propylene rubber with styrene, its derivative or, if necessary, another vinyl monomer in the presence of a cross-linked acrylic rubber or the like. Examples of them include polystyrene, high-impact polystyrene, AS resin, ABS resin, MBS resin, AES resin and AAS resin. These resins may be used either singly or in the form of a mixture of two or more of them.

The flame retardants can be used either singly or in the form of a mixture of two or more of them in the present invention.

The amount of the flame retardant is preferably as small as possible, since the mechanical properties of the composition are impaired as the amount of the additives is increased. The flame retardant is used in an amount of 3 to 50 parts by weight, preferably 6 to 35 parts by weight, for 100 parts by weight of the styrene resin. When its amount is less than 3 parts by weight, no sufficient flame retardancy can be obtained and, on the contrary, when it exceeds 50 parts by weight, the tensile strength and impact strength of the molding are reduced unfavorably.

The average particle size of antimony trioxide used in the present invention is 3 to 9 µm and preferably 4 to 7 µm. When it is less than 3 µm, the light resistance is seriously reduced and, on the contrary, when it exceeds 9 µm, the tensile strength and impact strength of the molding are reduced unfavorably, though an excellent light resistance is obtained.

The average particle size is determined herein by determining the particle size distribution with a centrifugal precipitation particle size distribution determination apparatus (SA-CP 3; mfd. by Shimadzu Corp.) by the liquid phase precipitation optical transmission method and calculating the particle size of cumulative 50% by weight on the basis of the distribution.

Antimony trioxide used as the flame retarding assistant is produced by any well-known process such as a process wherein a sodium carbonate solution of senarmontite or valentinite occurring in nature or antimony oxychloride formed by hydrolyzing antimony chloride is boiled or a process wherein metallic antimony is oxidized with air.

A plasticizer, heat stabilizer, light stabilizer, ultraviolet absorber, pigment, dye or reinforcement such as glass fibers, glass beads or asbestos can be incorporated into the styrene resin of the present invention, if necessary.

The flame-retardant styrene resin composition of the present invention can be produced by any of ordinary processes. For example, it can be produced by mixing all of the above-described components of the composition at once, melt-kneading the mixture with an extruder to form pellets and molding the pellets.

A flame-retardant styrene resin having an excellent light resistance can be provided according to the present invention.

The following Examples will further illustrate the present invention.

In the Examples, the performance tests were conducted by the following methods:

(Light resistance)

(1) Irradiation with light:

apparatus: xenon long-life fadeometer
irradiation energy: 4.0 mW/cm² (at 300nm~400nm)
temperature in the tank: 63°C
humidity in the tank: 50% RH

(2) Color difference:

Color difference (ΔE) was calculated by the following equation:

$$\Delta E = [(L_2-L_1)^2 + (a_2-a_1)^2 + (b_2-b_1)^2]^{1/2}$$

wherein:

L_1, a_1 and b_1 represent the reference lightness (L_1) and chromaticity (a_1 and b_1),
and L_2, a_2 and b_2 represent the lightness (L_2) and chromaticity (a_2 and b_2) after discoloration.

The smaller the color difference, the lower the extent of discoloration.

(Izod impact strength)

Izod impact strength was determined according to ASTM D 256.

(Flame resistance)

Underwriters' Laboratories (U.S.A.) standard:

The order of flame retardancy in the burning tests according to UL 94 (the third edition dated September 3, 1985) was V-0 > V-1 > V-2. No dropping occurred in V-0 and dropping occurred in V-2.

(Gloss)

The gloss was determined by the ASTM test method D 523.

Example 1

28 parts by weight of brominated bisphenol A epoxy resin (Pratherm EC-20; a product of Dainippon Ink & Chemicals, Inc.) and 7 parts by weight of antimony trioxide having an averege particle size of 4 μm were compounded into a mixture of 50 parts by weight of an ABS resin (40% of polybutadiene, 15% of acrylonitrile and 45% of styrene) and

50 parts by weight of an AS resin (30% of acrylonitrile and 70% of styrene) and melt-mixed with a 40 mm-diameter extruder (with a vent) kept at 220°C to form pellets. The pellets were injection-molded at 220°C to form a molding, which was subjected to the performance tests. The results are given in Table 1.

Examples 2 to 4

The same procedure as that of Example 1 was repeated except that antimony trioxide having an average particles size of 4 µm was replaced by antimony trioxide having an average particle size of 5.2 µm, 7.8 µm or 9 µm. The results of the performance tests are given in Table 1.

Example 5

The same procedure as that of Example 1 was repeated except that the brominated bisphenol A epoxy resin was replaced by 28 parts by weight of tetrabromobisphenol A carbonate oligomer (Fire Guard FG-7500; a product of Teijin Chemicals Ltd.) and antimony trioxide having an average particle size of 5.2 µm and that the extrusion temperature and injection-molding temperature were set at 200°C. The results of the performance tests are given in Table 2. Examples 6 and 7

The same procedure as that of Example 1 was repeated except that the brominated bisphenol A epoxy resin was replaced by 20 parts by weight of tetrabromobisphenol A, 20 parts by weight of bis(tribromophenoxy)ethane and 4 parts by weight of antimony trioxide having an average particle size of 5.2 µm. The results of the performance tests are given in Table 2.

Comparative Example 1

28 parts by weight of brominated bisphenol A epoxy resin (Pratherm EC-20) was compounded into 100 parts by weight of the same resin mixture as that of Example 1, and melt-mixed with a 40 mm-diameter extruder (with a vent) kept at 220°C to form pellets. The pellets were injection-molded at 220°C to form a molding, which was subjected to the performance tests. The results are given in Table 3 which indicates that the flame resistance is inferior when the amount of the flame retardant is same, though the light resistance is superior to that obtained when antimony trioxide was used together.

Comparative Example 2

The same procedure as that of Comparative Example 1 was repeated except that the amount of the brominated bisphenol A epoxy resin was altered to 37 parts by weight. The results of the performance tests are given in Table 3 which indicates that although the light resistance was superior to that obtained when antimony trioxide was used together, the amount of the flame retardant had to be increased to attain a flame resistance of V-0, which caused a serious reduction in the Izod impact strength.

Comparative Examples 3 to 5

The same procedure as that of Example 1 was repeated except that 7 parts by weight of antimony trioxide having an average particle size of 0.5 µm, 1 µm or 2 µm was used. The results of the performance tests are given in Table 3 which indicates that the light resistance was poor.

Comparative Example 6

The same procedure as that of Example 1 was repeated except that the brominated bisphenol A epoxy resin was replaced by a tetrabromobisphenol A carbonate oligomer (Fire Guard FG-7500; a product of Teijin Chemicals Ltd.) and antimony trioxide having an average parzicle size of 0.5 µm. The results of the performance tests are given in Table 4 which indicates that the light resistance was poor.

Comparative Example 7

The same procedure as that of Example 1 was repeated except that the brominated bisphenol A epoxy resin was replaced by 20 parts by weight of tetrabromobisphenol A and 4 parts by weight of antimony trioxide having an average particle size of 0.5 µm and that the extrusion temperature and injection molding temperature were set at 200°C. The results of the performance tests are given in Table 4, which indicates that the light resistance was poor.

Example 8

The same procedure as that of Example 1 was repeated except that antimony trioxide having an average particle diameter of 4 µm was replaced by antimony trioxide having an average paticle diameter of 4.5 µm. The results of the performance tests are given in Table 4.

Table 1

	Average particle size (μm)	Ex. 1	Ex. 2	Ex. 3	Ex. 4
Styrene resin		100	100	100	100
Brominated epoxy resin		28	28	28	28
Antimony trioxide	4	7			
Antimony trioxide	5.2		7		
Antimony trioxide	7.8			7	
Antimony trioxide	9				7
Combustibility (1/16")	–	V-0	V-0	V-0	V-0
Gloss (%)	–	89	87	87	85
Color difference (ΔE) (300 h)	–	22	20	15	143
Izod impact strength (kg-cm/cm)	–	17	15	11	10

Table 2

	Average particle size (μm)	Ex. 5	Ex. 6	Ex. 7
Styrene resin		100	100	100
Brominated epoxy resin				
TBA carbonate oligomer		28		
Tetrabromobisphenol A			20	
Bis(tribromophenoxy)ethane				20
Antimony trioxide	5.2	7	4	4
Combustibility (1/16")	–	V-0	V-2	V-2
Gloss (%)	–	87	89	88
Color difference (ΔE) (300 h)	–	18	13	11
Izod impact strength (kg-cm/cm)	–	13	18	19

Table 3

	Average particle size (μm)	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5
Styrene resin		100	100	100	100	100
Brominated epoxy resin		28	37	28	28	28
Antimony trioxide	0.5			7		
Antimony trioxide	1				7	
Antimony trioxide	2					7
Combustibility (1/16")	–	V-2	V-0	V-0	V-0	V-0
Gloss (%)	–	89	89	89	90	89
Color difference (ΔE) (300 h)	–	18	19	27	27	25
Izod impact strength (kg-cm/cm)	–	23	12	18	18	19

Table 4

	Average particle size (μm)	Comp. Ex. 6	Comp. Ex. 7	Ex.8
Styrene resin		100	100	100
TBA carbonate oligomer		28		
Tetrabromobisphenol A			20	
Brominated epoxy resin				28
Antimony trioxide	0.5	7	4	
Antimony trioxide	4.5			7
Combustibility (1/16")	-	V-0	V-2	V-0
Gloss (%)	-	90	90	88
Color difference (ΔE) (300 h)	-	25	20	20
Izod impact strength (kg-cm/cm)	-	19	26	15

Claims

1. A flame-retardant styrene resin composition comprising:

- 100 parts by weight of a styrene resin,
- 3 to 50 parts by weight of a halogen-containing flame retardant selected from the group consisting of a brominated bisphenol A epoxy resin, a tetrabromobisphenol A carbonate oligomer, tetrabromobisphenol A and bis(tribromophenoxy)ethane, and

- 0.5 to 15 parts by weight of antimony trioxide having an average size of from 3 to 9 µm.

2. The composition of claim 1, wherein the styrene resin is polystyrene, a homopolymer of a styrene compound or a copolymer of styrene or a styrene compound and a co-monomer.

Patentansprüche

1. Flammenhemmende Styrolharzzusammensetzung, umfassend:

   - 100 Gewichtsteile eines Styrolharzes,

   - 3 bis 50 Gewichtsteile eines Halogen enthaltenden Flammschutzmittels, ausgewählt aus der Gruppe, bestehend aus einem bromierten Bisphenol-A-Epoxyharz, einem Tetrabrombisphenol-A-Carbonat-Oligomer, Tetrabrombisphenol-A und Bis(tribromphenoxy)ethan, und

   - 0,5 bis 15 Gewichtsteile Antimontrioxid mit einer mittleren Teilchengröße im Bereich von 3 bis 9 µm.

2. Zusammensetzung nach Anspruch 1, worin das Styrolharz Polystyrol, ein Homopolymer aus einer Styrolverbindung oder ein Copolymer aus Styrol oder einer Styrolverbindung und einem Comonomer ist.

Revendications

1. Composition de résine styrène retardateur de flamme comprenant :

   - 100 parties en poids d'une résine styrène,
   - 3 à 50 parties en poids d'un retardateur de flamme contenant un halogène sélectionné parmi le groupe constitué par une résine époxy bisphénol A bromée, un carbonate de tétrabromobisphénol A oligomère, le tétrabromobisphénol A et le bis(tribromophénoxy)éthane, et
   - 0,5 à 15 parties en poids de trioxyde d'antimoine ayant une dimension moyenne comprise entre 3 et 9 µm.

2. Composition selon la revendication 1, dans laquelle la résine styrène est du polystyrène, un homopolymère d'un dérivé du styrène, ou un copolymère de styrène ou d'un dérivé du styrène et d'un comonomère.